Novel Hydrazone Based Hole Transport Materials for Electrophotography

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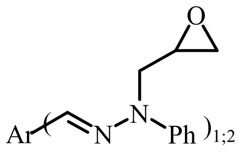
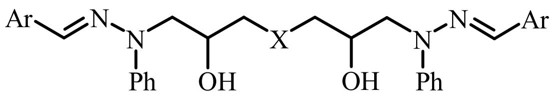
Abstract

Monomeric, dimeric and polymeric hydrazone based hole transporting materials (TM) with the following structures were developed and evaluated for electrophotography.



Monomeric structure



Dimeric structure

Polymeric structure

The general synthesis for all of these derivatives involves the reaction of the suitable aldehydes, having heterocyclic or aromatic chromophores (Ar), with the phenylhydrazine, followed by the reaction with epichlorohydrin. The dimeric and polymeric structures require an additional reaction step involving structures a-e (denoted as X above) to bind the hydrazone units into the dimeric structure or polymeric chain. The final products were purified several times and their structures were confirmed by ^{1}H-NMR, ^{13}C-NMR, and UV and IR spectra. The ionization potential (I_p) and hole mobility (using xerographic time of flight technique) were measured for all the compounds. The presence of oxiranyl or hydroxyl groups improves adhesion and compatibility not only with traditional polycarbonate (PC) binder material but also with polyvinylbutyral (PVB). Meanwhile, such dimeric or polymeric hole TM can be chemically cross-linked in the layer, for example, by reaction of the hydroxyl groups with polyisocyanates. Monomers with two oxiranyl groups can be cross-linked with polythiols. These TM properties increase the layer stability to bending, stretching and abrasion, as well as the effects of abrasion. The synthesized TM and compositions with binder exhibit good hole transporting properties and high mobility making them useful for preparation of high sensitivity electro-photographic photoconductors. They also can be used for preparation of bipolar transporting compositions and single layer photoreceptors.

Introduction

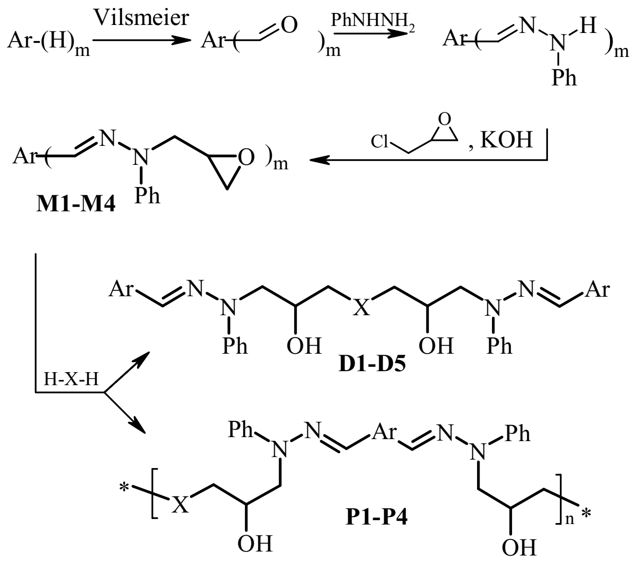
Organic charge-transporting materials are used in electrophotographic photoreceptors, light-emitting diodes, photovoltaic devices and other optoelectronic devices.[1,2] Rapid charge transporting ability, high photosensitivity, simple synthesis and low price are the advantages of the hydrazones against other charge TM.[3] Low molecular weight TM-containing hydrazone moieties are usually crystalline materials, are not capable of forming thin, neat homogenous layers, and must be used in combination with polymeric hosts. The presence of a large proportion of polymer host in the compositions, usually 50% of the total composition mass, leads to considerable decrease of carrier mobility. Even in such compositions, the possibility of the TM crystallization remains; this causes problems during electrophotographic layer (EPL) preparation and extended printing. From this point of view the low-molecular weight materials that form stable amorphous glasses having glass-transition temperatures above room temperature or photo-conducting polymers are superior to crystalline materials. Among the great number of studies devoted to low-molar-mass aromatic hydrazones only few glass-forming compounds[4-7] and polymers[9-11] with hydrazone moiety are reported.

Here we report on the synthesis, characterization and photoconductive properties of the novel hydrazone-based hole TMs in the form of monomeric, dimeric and polymeric structures. The general synthesis for all of these derivatives involves the reaction of the heterocyclic or aromatic aldehyde chromophores with the phenylhydrazine, followed by the reaction with epichlorohydrin. The dimeric and polymeric structures require an additional reaction step involving a group to bind hydrazone units into dimeric structure or polymeric chain. The ionization potential (I_p) and hole mobility (using xerographic time of flight technique) were measured for all the compounds. The presence of oxiranyl or hydroxyl groups improves adhesion and compatibility not only with traditional PC binder material but also with PVB. The synthesized TM and compositions with binder exhibit good hole transporting properties and high mobility making them useful for preparation of high sensitivity electro-photographic photoconductors.

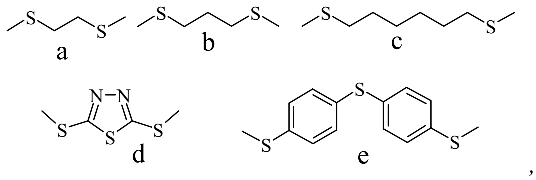
Experimental

Synthesis

The synthesis of the monomeric structures **M1-M4**, dimers **D1-D4** and polymers **P1-P4** possessing hydrazone moieties were done in the reaction sequence shown below:



where m is 1 or 2, the structures of the X group are



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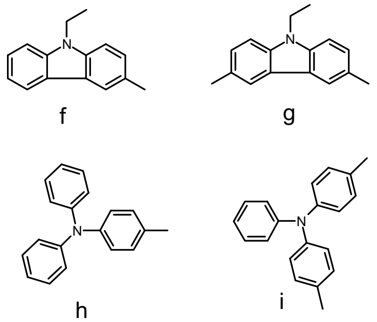
and those of the chromophores Ar are



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The first step was the Vilsmeier reaction followed by the reaction with phenylhydrazine. The next step was N-alkylation of hydrazone with epichlorohydrin in the presence of KOH and anhydrous Na_2SO_4 to give the monomeric compounds **M1**, **M2** or **M3**, **M4**. The dimers **D1-D5** were prepared by the reaction of dimercaptoalkanes with 2 equivalents of **M1** or **M2** in the presence of catalyst triethylamine (TEA). In the preparation of the polymers, poly-addition of monomers **M3**, **M4** with dimercapto compounds was carried out in the presence of TEA at the reflux of THF. The polymers **P1-P4** with hydrazone moieties were isolated. The final products were purified and their structures confirmed by ^{1}H-NMR, and UV and IR spectra.

Table 1. Composition and Parameters of the Hydrazone Based Hole TM

TM	X	Ar	m	T_m (°C)	T_g (°C)	I_P (eV)
M1	**-**	**f**	**1**	136-137	-	5.43
M2	**-**	**h**	**1**	141-142.5	-	5.43
M3	**-**	**g**	**2**	119-120	-	5.37
M4	**-**	**i**	**2**	163.5-165	-	5.35
D1	**a**	**f**	**-**	174*; 181*	69	5.30
D2	**a**	**h**	**-**	76*	45	5.39
D3	**b**	**f**	**-**	102*; 107*	73	5.33
D4	**b**	**h**	**-**	62*	54	5.43
D5	**c**	**h**	**-**	-	51	5.40
P1	**c**	**g**	**-**	-	79	5.39
P2	**d**	**g**	**-**	-	104	5.40
P3	**e**	**g**	**-**	-	131	5.40
P4	**e**	**i**	**-**	-	125	5.33

*Determined from DSC (first heating)

Measurements

Thermal transition data for synthesized dimers **D1**-**D5** and polymers **P1**-**P4** possessing hydrazone moieties was collected using a TA Instruments Model 2929 Differential Scanning Calorimeter (New Castle, DE) equipped with a DSC refrigerated cooling system (-70°C minimum temperature limit), and dry helium and nitrogen exchange gases. The calorimeter ran on a Thermal Analyst 2100 workstation with version 8.10B software. An empty aluminums pan was used as the reference. Samples of 4-7 mg as obtained from synthesis were heated in aluminums pans at a scan rate 10 K/min under a nitrogen flow. During the first heating the melting points were measured. After melting, the samples were cooled with the same rate. The resulting glasses were heated again under the same conditions to measure the glass transitions.

The average molecular weight and the molecular weight distribution were estimated by gel permeation chromatography (GPC) using a Waters GPC system including a Waters 410 UV detector (254 nm), four columns (300X7.5 mm) filled with PL-Gel absorbent (pore sizes: 10^6, 10^5, 10^4 and 5000 nm) using THF as eluant. Polystyrene standards were used for column system calibration.

Ionization potential was measured by the photoemission in air method described in Ref. 12.

The monomeric structures **M1**-**M4** are able to form homogenous layers only with polymeric binder, so samples for mobility measurements were prepared from 1:1 mass proportion compositions of these TM with various binders. The branched hydrazones **D1**-**D5** are able to form stable layers without binder, so samples for mobility measurements were prepared from neat **D1**-**D5** and from 1:1 mass proportion compositions of these TM with binders. Two types of polyvinylbutyral were used: PVB1 from Aldrich with average M_W = 70,000 – 100,000, PVB2 from Sekisui S-LEC B BX-1; and Polycarbonate-Z (PC-Z) (Iupilon Z-200 from Mitsubishi Gas Chemical Co.). All monomers and dimers investigated here form transparent layers with all these binders. In the case of film forming polymers **P1**-**P4** the samples for mobility measurements were prepared from solutions of neat materials using THF as the solvent. The sample substrate was polyester film with conductive Al layer. The layer thickness was in the range 5-10 µm. The cross-linked samples were prepared from composition of monomer **M4** and trithiocyanuric acid (TTR) from Aldrich at mass proportion 5:1. The samples were heated at 120°C for 0.5 h to cross-link. Three-component layers, capable to transport both holes and electrons, were prepared from the dimer **D2**, electron transporting material ST917 (SynTec-Synthon Chemicals GmbH) and PVB2 at mass proportion 4:2:1.

The hole drift mobility was measured by time of flight technique.[13-15] Positive corona charging created electric field inside the TM layer. Charge carriers were generated at the layer surface by illumination with pulses of nitrogen laser (pulse duration was 2 ns, wavelength 337 nm). The layer surface potential decrease as a result of pulse illumination was up to 1-5% of the initial potential before illumination. The capacitance probe that was connected to the wide frequency band electrometer measured the rate of the surface potential decrease, dU/dt. The transit time t_t was determined by the kink on the curve of the dU/dt transient in linear or double logarithmic scale. The drift mobility was calculated by the formula $\mu=d^2/U_0t_t$, where d is the layer thickness and U_0 is the surface potential at the moment of illumination.

Results and Discussion

The synthesized monomeric structures **M1**-**M4** are easy crystallized substances. The molecules of the synthesized hydrazone dimers **D1**-**D5** consist of two hydrazone branches linked by the central flexible bridge. The molecular structure of these TM makes crystallization in solid state difficult. Formation of the glassy state of the **D1**-**D5** was confirmed by DSC analysis. The melting points (T_m) and glass transition temperatures (T_g) of synthesized TM are presented in Table 1. These investigations revealed that some of the dimeric structures can exist both in crystalline and amorphous state while others were found only in amorphous phase in our experiments. The DSC curve for **D1** at first heating reveals a number of polymorphous changes before melting (Fig. 1). This means that there are two different crystalline forms of this TM with melting points at 174°C and 181°C and transitions of one into another take place during first heating. No crystallization takes place during cooling or second heating, only glass transition at 69°C is revealed in the second heating. This means that the material remains in glassy state after melting and subsequent cooling. This is a common feature for all the branched hydrazones investigated here. The glassy state of these materials is quite stable; no signs of crystallization was detected in the glassy layers during over a year storage at ambient conditions. Glass transition occurs at 51°C but no melting is seen for **D5** (Fig. 2), this means that the original state of the sample was amorphous. The comparison of the DSC analysis results for the **D1**-**D5** reveals a significant role of the fragment X. The structure of the charge transporting chromophores also has a significant influence on melting and glass transition points of the presented TM. These temperatures are lower for the dimers and polymer with triphenylamine chromophore as compared with carbazolyl, while the inverse result is in the case of monomeric structures **M1**-**M4**. In addition, the molecular mass (weight) also has significant influence on the thermal transition date, particularly for polymeric structures. Increasing the molecular mass of **P1**-**P5** increases the glass transition temperatures.

The average molecular weight and the molecular weight distribution of the polymers **P1**-**P4** detected by GPC are presented in Table 2. Increasing nucleophyllity of dimercapto compounds used in the poly-addition reaction obviously increases molecular weight of the polymers.

Table 2. Molecular Mass Data of Polymers P1-P4.

TM	M_n	Mw	M_w/M_n
P1	700	1600	2.3
P2	2500	12000	4.8
P3	8500	73000	8.6
P4	10000	85000	8.5

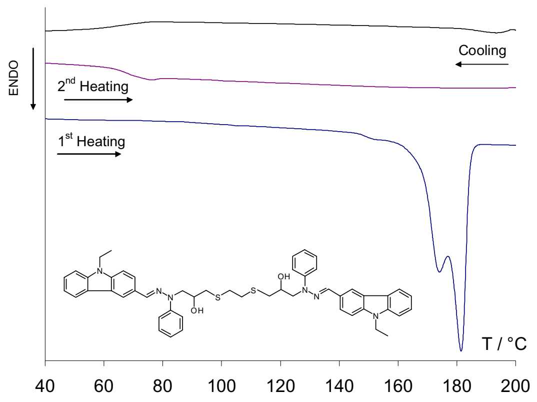

*Figure 1. DSC curves of **D1**(heating and cooling rate 10 K/min).*

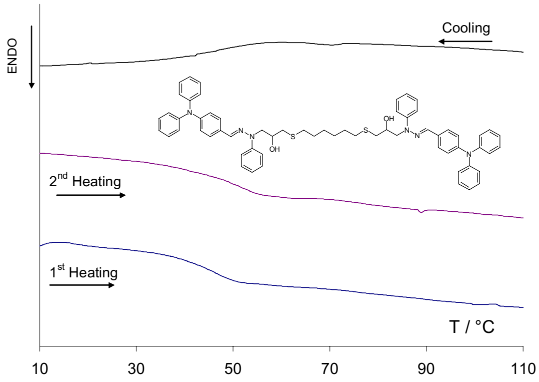

Figure 2. DSC curves of D5)(heating and cooling rate 10 K/min).

The ionization potential values are presented in Table 1 and examples of photoemission spectra are given in Fig. 3. There is little ionization potential (I_p) difference depending on the group **X**; the charge transporting hydrazone groups are determining its value. This is also seen on Fig. 3, on which photoemission in air spectra for the polymers investigated are presented. In the cases of the polymers **P1, P2** and **P3** with carbazole containing dihydrazone ionization potential is near to 5.40 eV while it is 5.33 eV for the polymer **P4** with triphenylamine group.

Examples of xerographic time of flight transients are seen on Fig. 4. The mobility investigation results are given in Table 3 and on Fig. 5 – 7. In Table 3 the zero field mobility μ_0, mobility value at $6.4\cdot10^5$ V/cm electric fields as well as Pool-Frenkel parameter α, according to formula (1), are given.

$$\mu = \mu_0 e^{\alpha\sqrt{E}} \quad (1)$$

The mobility field dependencies are well approximated by formula (1) in all the cases.

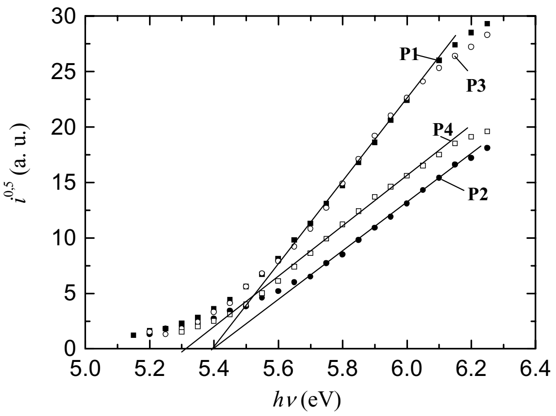

Figure 3. Photoemission in air spectra of polymeric TM.

Table 3. Mobility Data

Layer composition	μ_0 (cm^2/V·s)	μ (cm^2/V·s)	α (cm/V)$^{0.5}$
M1 + PVB1	$5.5\cdot10^{-9}$	$4.6\cdot10^{-7}$	0.0055
M2 + PVB1	$9\cdot10^{-8}$	$1.7\cdot10^{-6}$	0.0039
M2 + PVB2	$2\cdot10^{-7}$	$1\cdot10^{-5}$	0.0050
M3 + PC-Z	$\sim1\cdot10^{-7}$	$1.5\cdot10^{-5}$	~0.006
M3 + PVB2	$3.3\cdot10^{-8}$	$3.6\cdot10^{-6}$	0.0059
M4 + PVB1	$3.7\cdot10^{-7}$	$2.2\cdot10^{-6}$	0.0022
M4 + (PC-Z), 4:6	$1.1\cdot10^{-6}$	$3.6\cdot10^{-5}$	0.0044
M4 + TTR, 5:1	$3\cdot10^{-8}$	$5\cdot10^{-6}$	0.0064
D1	$1\cdot10^{-7}$	$3.5\cdot10^{-5}$	0.007
D1 + PVB1	$7\cdot10^{-9}$	$1.2\cdot10^{-6}$	0.0064
D2	$3.8\cdot10^{-6}$	$1\cdot10^{-4}$	0.0040
D2 + PC-Z	$2.5\cdot10^{-7}$	$7.3\cdot10^{-6}$	0.0042
D2 + PVB1	$4\cdot10^{-8}$	$2.5\cdot10^{-6}$	0.0051
D2 + ST917 + PVB2, 4:2:1; holes	$1.6\cdot10^{-7}$	$7.3\cdot10^{-6}$	0.0048
D2 + ST917 + PVB2, 4:2:1; electrons	$1.1\cdot10^{-9}$	$2.3\cdot10^{-8}$	0.0038
D3	$1.2\cdot10^{-7}$	$4.5\cdot10^{-5}$	0.0074
D3 + PVB1	$2\cdot10^{-9}$	$4\cdot10^{-7}$	0.0067
D4	$4.5\cdot10^{-6}$	$1.2\cdot10^{-4}$	0.0041
D4 + PVB1	$1.3\cdot10^{-7}$	$5\cdot10^{-6}$	0.0046
D5	$3.8\cdot10^{-6}$	$2\cdot10^{-4}$	0.0050
D5 + PVB1	$7.5\cdot10^{-8}$	$2.2\cdot10^{-6}$	0.0042
P1	$1.3\cdot10^{-7}$	$8.6\cdot10^{-6}$	0.0052
P2	$1.8\cdot10^{-7}$	$1.7\cdot10^{-5}$	0.0057
P3	$1.5\cdot10^{-7}$	$3.2\cdot10^{-5}$	0.0067
P4	$2.8\cdot10^{-6}$	$1.9\cdot10^{-4}$	0.0053

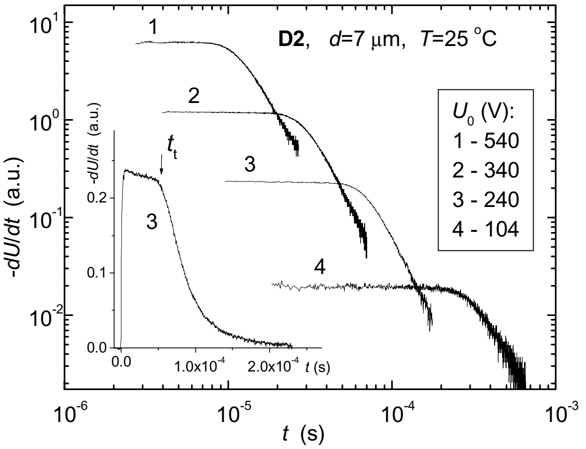

Figure 4. Xerographic time of flight transients for neat dimer D2.

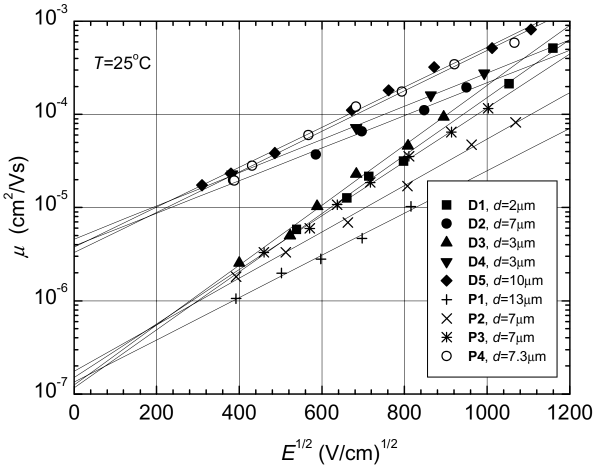

Figure 5. Hole mobility field dependencies for the TM investigated.

A number of conclusions may be made from the results presented. First of all, the mobility value is dependent on the hydrazone group structure. So, hole mobility is higher in the case of dihydrazone monomers **M3** and **M4** as compared with simple hydrazones **M1** and **M2**. This may be regarded as obvious result of the conjugated system size. On the other hand, mobility is higher in the TM with triphenylamine group as compared with carbazole ring. The influence of these factors is obvious not only in monomers, but also in dimers and polymers.

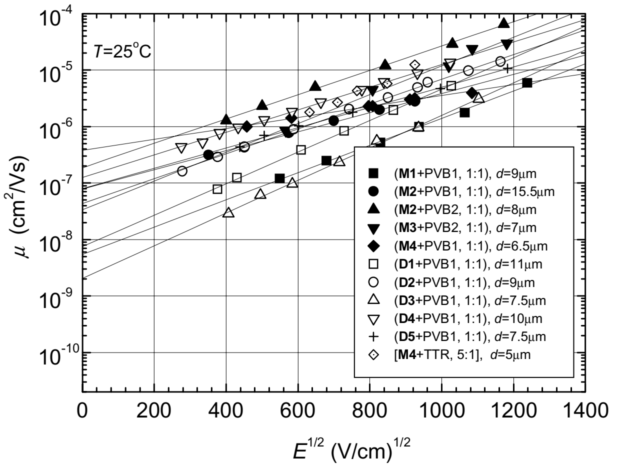

Figure 6. Hole mobility field dependencies for the compositions with TM investigated.

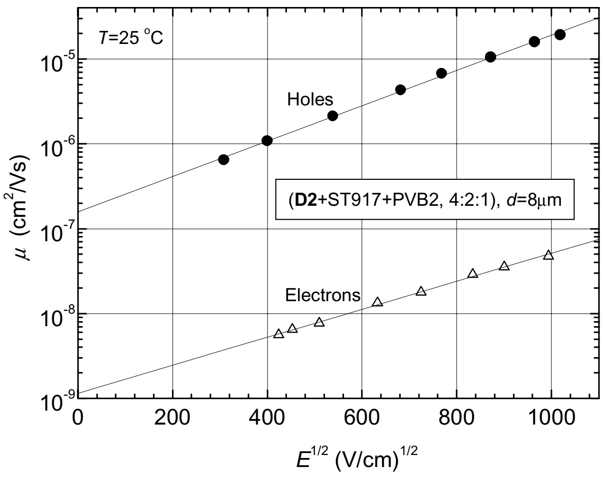

Figure 7. Hole and electron mobility field dependencies for the bipolar composition of D2, ST917 and PVB2.

Another important factor, influencing mobility in the real transporting composition is presence and concentration of binder material (BM) in it. So dimer TM investigated here, and especially polymers, may be used in neat form, without BM, for layer preparation. As seen from the results presented, mobility is highest in the neat dimers as compared to composition of these dimers with BM. Usually; PVB reduces mobility more than PC. The results of Table 3 confirm this observation. The hole mobility in neat dimers, as well as in polymers, in the case of hydrazone groups with triphenylamine, reaches or exceeds 10^{-4} cm^2/V·s.

An example of cross-linked layer, made of the diepoxide **M4** and trithiocyanuric acid, demonstrates that high mobility may be realized in such compositions (Fig. 6). The cross-linked hole-transporting layer is insoluble in organic solvents, such as THF, and is stable to bending, stretching and abrasion.

The TM investigated here may also be used for preparation of the composition with bipolar transporting properties. An example of such compositions described here is the three-component composition of the dimer **D2**, electron transporting material ST917 and PVB2 as binder material (Fig. 7). The mobility parameters of both holes and electrons in such composition enable to use them for preparation of single layer photoreceptors.

According to widely used charge transport models in molecularly doped polymers mobility and its field dependence are determined by the energetic and positional disorders in the transporting composition. The mobility data in the molecular solids are usually interpreted in terms of the Borsenberger, Pautmeier and Bässler formula:[16]

$$\mu(E,T) = \mu_0{}' \exp\left[-\left(\frac{2\sigma}{3kT}\right)^2\right] \exp\left\{C\left[\left(\frac{2\sigma}{3kT}\right)^2 - \Sigma^2\right]E^{1/2}\right\}. \quad (2)$$

Here, μ is the mobility, σ is the energy width of the hopping site manifold, which provides a measure of the energetic disorder, Σ is the degree of positional disorder, E the electric field, $\mu_0{}'$ is a mobility pre-factor. It is evident from this formula that the zero field mobility $\mu(0,T)$ is determined by the energetic disorder σ, while mobility field dependence is caused by the difference between the energetic disorder σ and positional disorder Σ dependent terms in the formula. Our data may be interpreted of the basis of this model.

Conclusions

Monomeric, dimeric and polymeric hydrazone based hole transporting materials were synthesized and investigated as potential new materials for electrophotography. The monomeric epoxides and diepoxides may not only used as conventional hole transporting materials, but also allow to synthesize dimer and polymer structures. The monomers with two oxiranyl groups can be cross-linked with polythiols. These TM properties enable to increase the layer stability to bending, stretching and abrasion, as well as the effects of liquid developer. The molecular structure of the dimeric structures prevents TM crystallization, allows the preparation of stable films without binder material or with a low binder concentration, and is compatible with polycarbonate and polyvinylbutyral binders. The polymer materials may be of particular interest for development of future electro-photographic photoreceptors. The hydroxyl groups allow for cross-linking of these transporting materials in the layer. The hole mobility of both neat TM and compositions with binder materials have been studied. The highest hole mobility, reaching 10^{-4} cm^2/Vs at $6{\cdot}10^5$ V/cm electric field, was observed in the neat dimeric and polymeric materials with triphenylamine moieties.

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Biographies

Dr. Nusrallah Jubran received his M.S degree in Chemistry from the Weismann Institute at Rehovot, Israel, and a Ph.D. in Chemistry from Ben-Gurion University at Beer-Sheva, Israel. He is currently a senior staff chemist in Samsung Digital Printing Solution Lab in Woodbury, MN. His current research activities focus on the development and scale up of novel OPC materials for electrophotography and is an IS&T member. njubran@mn.sisa.samsung.com

Dr. Vytautas Getautis studied chemical technology at Kaunas University of Technology, Lithuania. As an associate Professor at the Department of Organic Chemistry of Kaunas University of Technology, his research interests include the synthesis and properties of photoconductive molecular glasses and investigation of the products of the interaction of aromatic amines and heterocyclic compounds with epichlorohydrin. He published 5 patents and 17 scientific papers.